Absorption correction: none
1839 measured reflections
1666 independent reflections
1150 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.026$

3 standard reflections
every 150 reflections
intensity decay: 0.40%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.241$ e Å^{-3}
$R(F) = 0.038$	$\Delta\rho_{min} = -0.224$ e Å^{-3}
$wR(F^2) = 0.104$	Extinction correction: none
$S = 1.111$	Scattering factors from
1666 reflections	*International Tables for*
158 parameters	*Crystallography* (Vol. C)
H atoms treated by a	Absolute configuration:
mixture of independent	ascertained from the
and constrained refinement	known configuration
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$	of the D-2-deoxyribose
where $P = (F_o^2 + 2F_c^2)/3$	substrate
$(\Delta/\sigma)_{max} < 0.001$	Flack (1983) parameter = 0.3 (17)

Table 1. *Hydrogen-bonding geometry* $(\text{Å}, \degree)$

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O7$'^i$	0.83 (3)	1.93 (3)	2.749 (3)	169 (3)
O8$'$—H8$'\cdots$O7$''$	0.79 (5)	2.12 (5)	2.798 (4)	145 (6)
O7$'$—H7$'\cdots$O8$'^{iii}$	0.70 (5)	2.00 (5)	2.693 (3)	168 (5)
C5$'$—H5$'a\cdots$O6^{iv}	0.97	2.56	3.507 (4)	166

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, -z$; (ii) $1 - x, y - \frac{1}{2}, -z$; (iii) $x, y - 1, z$; (iv) $2 - x, \frac{1}{2} + y, -z$.

The H2, H7$'$ and H8$'$ atoms were refined isotropically. All other H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

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Quininium (S)-Mandelate†

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Abstract

The structure of the title compound, $C_{20}H_{25}N_2O_2^+$.-$C_8H_7O_3^-$, at 122 (1) K has been compared to those of the closely related cinchonidinium mandelate salts [Gjerløv & Larsen (1997). *Acta Cryst.* B53, 708–718]. The hydrogen-bonding arrangement of infinite chains of alternating anions and cations is identical to the hydrogen-bonding pattern seen in the diastereomeric mandelate salts of cinchonidine. Likewise, the herring-

† Alternative name: 6$'$-methoxycinchonidin-1-ium α-hydroxybenzene-acetate.

bone stacking of the quinoline ring systems of the cations resembles the packing pattern observed in other salts of the cinchona alkaloids and in the free bases.

Comment

The optical resolution of racemates is often achieved through the formation of diastereomeric salts. Quinine and mandelic acid are commonly used as resolving agents for racemic acids and bases, respectively. The structure of the title compound, (I), has been investigated to gain insight into the chiral discrimination that takes place on formation of diastereomeric salts. The structure is compared to those of the mandelate salts of cinchonidine, a related cinchona alkaloid, which have been investigated earlier (Gjerløv & Larsen, 1997). As shown in the scheme below, quinine and cinchonidine differ only in the substituent at the C12 position. The H atom in cinchonidine is replaced by a methoxy group in quinine.

(I)

Quinine: $X = OCH_3$
Cinchonidine: $X = H$
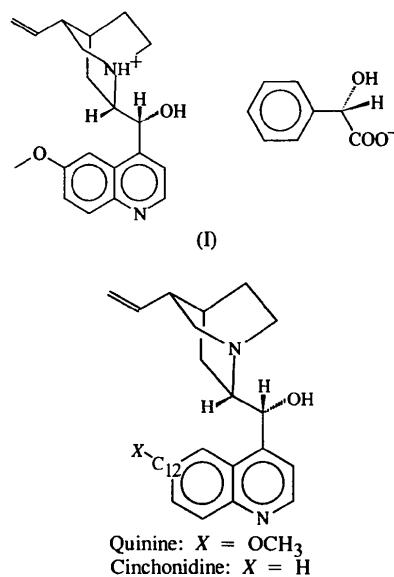
Apart from the obvious differences related to the methoxy group, the quininium cation, shown in Fig. 1, is almost identical to the cations found in the cinchonidinium mandelate salts (Gjerløv & Larsen, 1997). The most significant difference is a slight change in the O4—C18—C19—N2 torsion angle from −80 to −84°. This has the effect of moving the two hydrogen-bond donors further away from each other. A more skewed conformation of the quinuclidine system is also observed. In line with the stereochemical characterization employed by Oleksyn, Lebioda & Ciechanowicz-Rutkowska (1979) for cinchonine, the torsion angles about the N2–C21 line are suitable to illustrate differences in conformation. In the quininium salt, they deviate more from the idealized 0 and 120°. The torsion angle C24—C25—C26—C27 describes the orientation of the vinyl group,

which is the most flexible part of the cation. The value of 114.2 (2)° is close to the most frequently observed value of around 120° (Gjerløv & Larsen, 1997). The geometry of the quininium ion compares well with the structures of the cinchonidinium cation observed in the two diastereomeric mandelate salts.
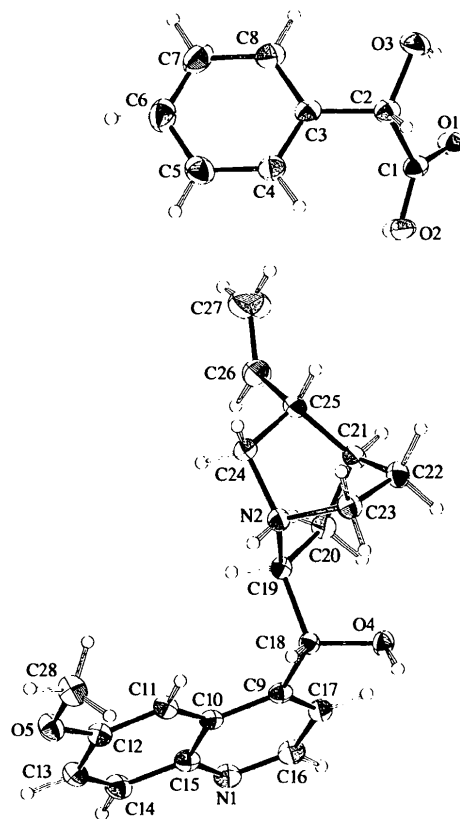
Fig. 1. Molecular structure of the mandelate anion (top) and the quininium cation (bottom) showing 50% probability displacement ellipsoids for the non-H atoms. The H atoms are shown as spheres of fixed radii.

The conformation of the anion shown in Fig. 1 is described by the two torsion angles O1—C1—C2—O3 and O3—C2—C3—C4; the values for these angles in quininium (S)-mandelate are −5.13 (15) and −166.93 (10)°, respectively. They are within the range of values found in a previous study of the geometry of the mandelate anion in 23 mandelate structures (Larsen & Lopez de Diego, 1993). The intramolecular hydrogen bond O3—H3O···O1 observed in the present structure is also observed in 13 of the 23 structures.

In the cinchonidinium mandelate structures, an elongation is observed of the C—O bond of the carboxylate group which involves the O atom that is hydrogen bonded to the positively charged cation. We do not observe the same trend in the present structure. This variation could be caused by an increased strength of the

intramolecular hydrogen bond O3—H3O⋯O1, as reflected in the shorter O3⋯O1 distance of 2.5857 (12) Å (Table 2). This distance is 2.592 (2) Å in cinchonidinium (S)-mandelate, and 2.597 (2) and 2.640 (2) Å in the two independent anions of cinchonidinium (R)-mandelate. In the latter anion, the O3—C2—C1—O1 moiety deviates most from planarity. Also, the two intermolecular hydrogen bonds are slightly shorter than the average values found in the cinchonidinium salts.

The packing of the molecules resembles the packing found in the cinchonidinium mandelates, with infinite hydrogen-bonded chains of alternating anions and cations formed along the shortest crystallographic axis, of ca 6.4 Å (Fig. 2). The quinoline moieties adopt the same herring-bone pattern as was found in the cinchonidinium salts, the interplanar angle being 62°, calculated using PLATON (Spek, 1990). Considering the similarity between quinine and cinchonidine, one would have expected a similarity between the packing of the (S)-mandelate salts of quinine and cinchonidine. In contrast, we find that the packing arrangement in quininium (S)-mandelate resembles more the packing in cinchonidinium (R)-mandelate. In these two salts, the anions pack in a head-to-tail arrangement in the direction of a ca 12 Å axis, as seen in Fig. 2. The only difference is that the direction of the head-to-tail arrangement is reversed due to the opposite chirality of the ions.
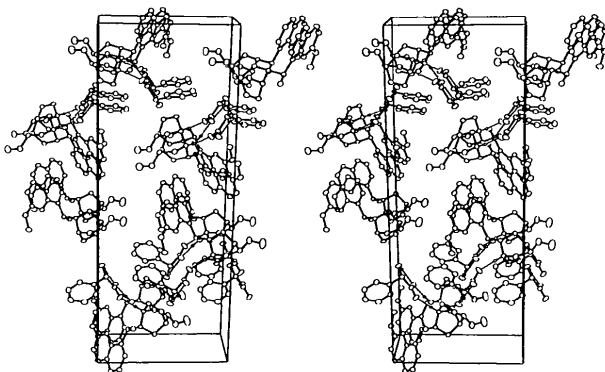

Fig. 2. Stereoscopic view of the crystal packing viewed along the a axis, showing the infinite hydrogen-bonded chains of alternating anions and cations. Hydrogen bonds are represented as thin lines. The b axis is horizontal and the c axis is vertical.

The packing of cinchonidinium (S)-mandelate is more dense; in this structure, the anions form a herring-bone stacking of the phenyl groups. Apart from the substituent at C12, which is a methoxy group in quinine and a hydrogen in cinchonidine, quininium (S)-mandelate is identical to cinchonidinium (S)-mandelate. The methoxy group causes the cations to move further apart in the direction of the 12.5 Å axis maintaining the herring-bone packing of the cations. The anions have adapted to the more spacious arrangement of the cations by replac-

ing the more dense head-to-head herring-bone stacking of the phenyl groups in cinchonidinium (S)-mandelate by a less dense head-to-tail packing in quininium (S)-mandelate. The herring-bone stacking of the cations is also found in the structure of quininium salicylate monohydrate (Oleksyn & Serda, 1993), though the cations and anions form discrete hydrogen-bonded ion pairs in this compound.

Experimental

Crystal data

$C_{20}H_{25}N_2O_2^+ \cdot C_8H_7O_3^-$	Cu $K\alpha$ radiation
$M_r = 476.56$	$\lambda = 1.54184$ Å
Orthorhombic	Cell parameters from 18
$P2_12_12_1$	reflections
$a = 6.5362 (6)$ Å	$\theta = 38.13–46.79°$
$b = 12.4737 (12)$ Å	$\mu = 0.674$ mm^{-1}
$c = 32.056 (3)$ Å	$T = 122 (1)$ K
$V = 2613.5 (4)$ Å^3	Needle
$Z = 4$	$0.4 \times 0.1 \times 0.1$ mm
$D_x = 1.211$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.008$
diffractometer	$\theta_{max} = 74.91°$
$\omega–2\theta$ scans	$h = 0 \rightarrow 8$
Absorption correction: none	$k = 0 \rightarrow 15$
6294 measured reflections	$l = -39 \rightarrow 40$
5290 independent reflections	3 standard reflections
5055 reflections with	frequency: 166.7 min
$I > 2\sigma(I)$	intensity decay: 3.7%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.213$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{min} = -0.207$ e Å^{-3}
$wR(F^2) = 0.071$	Extinction correction:
$S = 1.059$	SHELXL93 (Sheldrick,
5290 reflections	1993)
413 parameters	Extinction coefficient:
Only coordinates of H atoms	0.0035 (2)
refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2$	International Tables for
$+ 0.3863P]$	Crystallography (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute configuration:
$(\Delta/\sigma)_{max} = -0.043$	Flack (1983)
	Flack parameter = 0.08 (11)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.2533 (15)	C9—C17	1.371 (2)
O2—C1	1.2486 (15)	C9—C10	1.425 (2)
O3—C2	1.4199 (14)	C9—C18	1.5254 (15)
C1—C2	1.541 (2)	C10—C15	1.4239 (14)
C2—C3	1.517 (2)	C10—C11	1.428 (2)
C3—C8	1.393 (2)	C11—C12	1.374 (2)
C3—C4	1.394 (2)	C12—C13	1.419 (2)
C4—C5	1.388 (2)	C13—C14	1.359 (2)
C5—C6	1.390 (2)	C14—C15	1.417 (2)

C6—C7	1.384 (2)	C16—C17	1.411 (2)
C7—C8	1.393 (2)	C18—C19	1.5465 (15)
O4—C18	1.4162 (13)	C19—C20	1.5424 (15)
O5—C12	1.3614 (15)	C20—C21	1.537 (2)
O5—C28	1.4290 (15)	C21—C22	1.530 (2)
N1—C16	1.316 (2)	C21—C25	1.541 (2)
N1—C15	1.370 (2)	C22—C23	1.533 (2)
N2—C24	1.5005 (15)	C24—C25	1.544 (2)
N2—C23	1.5060 (14)	C25—C26	1.498 (2)
N2—C19	1.5065 (13)	C26—C27	1.317 (2)
C1—O1—O3	68.49 (7)	O5—C12—C11	125.67 (10)
C2—O3—O1	65.38 (6)	O5—C12—C13	113.37 (11)
O2—C1—O1	126.86 (11)	C11—C12—C13	120.96 (11)
O2—C1—C2	117.08 (11)	C14—C13—C12	120.00 (11)
O1—C1—C2	116.06 (10)	C13—C14—C15	121.13 (11)
O3—C2—C3	112.05 (10)	N1—C15—C14	117.54 (10)
O3—C2—C1	109.89 (10)	N1—C15—C10	123.36 (11)
C3—C2—C1	110.28 (9)	C14—C15—C10	119.11 (11)
C8—C3—C4	119.19 (12)	N1—C16—C17	124.19 (11)
C8—C3—C2	120.95 (12)	C9—C17—C16	119.79 (11)
C4—C3—C2	119.86 (11)	O4—C18—C9	111.27 (9)
C5—C4—C3	120.70 (12)	O4—C18—C19	109.95 (9)
C4—C5—C6	119.83 (14)	C9—C18—C19	107.44 (8)
C7—C6—C5	119.80 (13)	N2—C19—C20	107.73 (9)
C6—C7—C8	120.54 (13)	N2—C19—C18	111.80 (8)
C7—C8—C3	119.93 (13)	C20—C19—C18	114.50 (9)
C12—O5—C28	116.98 (9)	C21—C20—C19	110.02 (9)
C16—N1—C15	116.95 (10)	C22—C21—C20	109.38 (9)
C24—N2—C23	109.30 (9)	C22—C21—C25	107.53 (10)
C24—N2—C19	108.85 (8)	C20—C21—C25	110.43 (9)
C23—N2—C19	113.06 (9)	C21—C22—C23	109.09 (9)
C17—C9—C10	118.36 (10)	N2—C23—C22	108.89 (9)
C17—C9—C18	120.09 (10)	N2—C24—C25	110.00 (9)
C10—C9—C18	121.50 (10)	C26—C25—C21	113.58 (11)
C15—C10—C9	117.30 (10)	C26—C25—C24	111.66 (10)
C15—C10—C11	119.04 (10)	C21—C25—C24	107.24 (9)
C9—C10—C11	123.67 (10)	C27—C26—C25	124.2 (2)
C12—C11—C10	119.73 (10)		
O1—C1—C2—O3	−5.13 (15)	C25—C21—N2—C24	7.11 (8)
O1—C1—C2—C3	118.87 (12)	C25—C21—N2—C19	125.10 (8)
C1—C2—C3—C4	70.32 (14)	C25—C21—N2—C23	−112.06 (8)
O3—C2—C3—C4	−166.93 (10)	C20—C21—N2—C19	3.54 (7)
C10—C9—C18—O4	159.14 (10)	C20—C21—N2—C23	126.38 (9)
C17—C9—C18—O4	−23.61 (14)	C20—C21—N2—C24	−114.45 (9)
C17—C9—C18—C19	96.79 (12)	C22—C21—N2—C23	5.67 (8)
C10—C9—C18—C19	−80.45 (12)	C22—C21—N2—C24	124.84 (9)
C9—C18—C19—N2	154.64 (9)	C22—C21—N2—C19	−117.17 (9)
C9—C18—C19—C20	−82.49 (11)	C24—C25—C26—C27	114.2 (2)
O4—C18—C19—C20	38.75 (11)	C11—C12—O5—C28	−3.1 (2)
O4—C18—C19—N2	−84.12 (11)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O4—H4O···O1ⁱ	1.72 (2)	2.6711 (12)	174 (1)
N2—H2N···O2ⁱⁱ	1.70 (2)	2.6239 (13)	167 (2)
O3—H3O···O1	1.94 (2)	2.5857 (12)	129 (1)

Symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

All H atoms were located in difference Fourier calculations after refinement of the non-H atoms.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: DREADD (Blessing, 1987). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: OR-TEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1027). Services for accessing these data are described at the back of the journal.

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6α-Hydroxyvouacapan-7β,17β-lactone†

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Abstract

In the crystal structure of the title compound, $C_{20}H_{26}O_4$, adjacent molecules are linked through hydrogen bonds in an infinite chain structure in the [100] direction.

† Alternative name: 4b,6a,7,7a,8,9,10,11,11a,11b,11c,12-dodecahydro-7-hydroxy-8,8,11a-trimethylphenanthro[3,2-b:10.10a,1-bc]difuran-5(5H)-one.

Comment

6α-Hydroxyvouacapan-7β,17β-lactone (HVL) is a synthetic derivative of 6α,7β-dihydroxyvouacapan-17β-oic acid (ADV), which was isolated from the fruits of *Pterodon polygalaeflorus* Benth, as reported by Mahajan & Monteiro (1973). Both compounds showed anti-